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## Valence 2084

## Claims:

- 1. A lithium ion battery which comprises a positive electrode and a negative electrode; said positive electrode having an active material represented by the formula  $\mathrm{Li_aM'}_{(2-b)}\mathrm{M''}_b\mathrm{P}_3\mathrm{O}_{12-c}\mathrm{Z}_c$ ,  $0 \le b \le 2$ , 0 < c < 12, a is greater than zero and selected to represent the number of Li atoms to balance said formula; where M' and M' are the same or different from one another and are each elements selected from the group consisting of metal and metalloid elements; and where Z is a halogen.
  - The battery of claim 1 wherein the halogen is F (fluorine).
  - 3. The battery of claim 1 wherein said active material is represented by the formula  $\text{Li}_2\text{M}'_{(2-b)}\text{M}''_b\text{P}_3\text{O}_{12-c}\text{F}_c$ ; M' is selected from the group consisting of: V, Fe, Mn, and M' is selected from the group consisting of: V, Fe, Mn, Ti, Cr, Co, Ni, Cu, and Mo.
- 4. The battery of claim 1 wherein said active material is represented by one of the following formulas  $\text{Li}_{2.0}\text{M}'_{(2-b)}\text{M}''_bP_3O_{11.5}F_{0.5};$   $\text{Li}_{3}\text{M}'_{(2-b)}\text{M}''_bP_3O_{11.5}F_{0.5};$  and  $\text{Li}_{3}\text{M}'_{(2-b)}\text{M}''_bP_3O_{11}.$
- 5. The battery of claim 1 wherein said positive electrode active material is selected from the group consisting of: Li<sub>2.5</sub>V<sup>3+</sup>1.0<sup>3</sup>\*1.0<sup>3</sup>\*1.0<sup>3</sup>\*0.1.5<sup>5</sup>0.5; Li<sub>2.0</sub>V<sup>3+</sup>1.0<sup>3</sup>\*1.0<sup>3</sup>\*0.1.5<sup>5</sup>0.5; Li<sub>2.0</sub>V<sup>3+</sup>0.5<sup>5</sup>\*1.5<sup>5</sup>\*0.1.0<sup>5</sup>\*.
  Li<sub>2.0</sub>V<sup>3+</sup>0.5<sup>5</sup>\*1.5<sup>5</sup>\*0.1.0<sup>5</sup>; Li<sub>2.5</sub>V<sup>3+</sup>1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.5; Li<sub>2.0</sub>V<sup>3+</sup>0.5<sup>5</sup>\*0.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.1.5<sup>5</sup>\*0.

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- 6. The battery of claim 1 wherein  $M^\prime$  and  $M^{\shortparallel}$  are the same transition metal or are different transition metals.
- 7. The battery of claim 1 wherein at least one of M' and M" is selected from the group of transition metals.
- 8. The battery of claim 1 wherein M' and M'' are metals or metalloids independently selected from the group consisting of: V, Fe, Mn, Ti, Cr, Co, Ni, Cu, Mo, Al, Mg, Ca, B, Zn, Sn.
  - 9. The battery of claim 1 wherein said positive electrode active material is represented by the formula  $\text{Li}_{2}M'_{(2-b)}M''_{b}P_{3}O_{12-c}F_{c}$ ; M'and M" each have a valence state which is the same or different, where said valence state is +2 or +3.
  - 10. The battery of claim 1 wherein said positive electrode active material is characterized by deintercalating lithium ions during charging cycle of said battery; said negative electrode active material characterized by intercalating said deintercalated lithium ions during said charging cycle, and by subsequent deintercalation of lithium ions during discharge cycle; and said positive electrode active material further characterized by reintercalating said discharge cycle lithium ions.
  - 11. An electrochemical cell having an electrode which comprises an active material represented by the following formula:
- 35  $\text{Li}^{*1}_{(a-x)}$   $\text{MII}^{d}_{(2-b)}$   $\text{MII}^{e}_{b}$   $\text{P}^{*5}_{3}$   $\text{O}^{-2}_{12-c}$   $\text{Z}^{-1}_{c}$ ;

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(A) where each superscript value represents the oxidation states of respective elements in a first condition, x=0:

Superscript +1 is the oxidation state of one atom of Li (lithium),

Superscript d is the oxidation state of one atom of  $\ensuremath{\mathsf{MI}}$  ,

Superscript  $\ensuremath{\mathbf{e}}$  is the oxidation state of one atom of MII,

Superscript -1 is the oxidation state of one atom of Z which is a halogen,

Superscript +5 is the oxidation state of one atom of P (phosphorus) and in the case of  $P_3$  constitutes a total of 15,

Superscript -2 is the oxidation state of one atom of O (oxygen);

- (B) MI and MII are the same or different and are each elements independently selected from the group of metal and metalloid elements;
- (C) a, c, d and e are each greater than zero; d and e are each at least one;  $0 \le b \le 2$ ; c is less than 12; and where a, b, c, d and e fulfill the requirement: (a x 1) + ((2 b) x d) + (b x e) + 15 = (1 x c) + ((12 c) x 2); and
- (D) in a second condition represented by said formula with 0 < x ≤ a, and in said second condition, said oxidation state of MI is represented by d' and said oxidation state of MII is represented by e', said amount X of Li is removed from said compound, accompanied by a change in oxidation state of at least one of said MI and MII, according to ((2-b) x (d'-d)) + (b(e'-e)) = X; 35 where d' ≥ d and e' ≥ e; and where d, d', e, and e' are each less than or equal to 8.</p>

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- 12. The battery of claim 11 wherein the halogen is F (fluorine).
- 13. The cell according to claim 11 wherein d 5 and e are each at least 2, 0 s b s 2, and d, d', e, and e' are each less than or equal to 6.
  - 14. The cell according to claim 11 wherein d, d', e and e' are each less than or equal to 7; and at least one of the following two conditions are met: (1) d' > d and (2) e' > e.
    - 15. The cell according to claim 11 wherein MI and MII are each independently selected from the group consisting of: V, Fe, Mn, Ti, Cr, Co, Ni, Cu, Mo, Al, Mg, Ca, B, Zn, Sn.
    - 16. An electrode having an active material in a first condition represented by the formula  $\mathrm{Li}_{3-x}\mathrm{E}'_{(2-b)}\mathrm{E}''_b p_3 O_{12-c}\mathrm{F}_c$ , x=0,  $0 \le b \le 2$ , 0 < c < 12; where at least one of E' and E" is an element selected from the group consisting of metals and metalloids; and E' and E" are the same or different from one another; and in a second condition by said formula where  $0 < x \le 3$ ; and where at least one of E' and E" has an oxidation state higher than its oxidation state in said first condition.
- 17. An electrode which comprises an active material, represented by the nominal general formula 30 Li<sub>\*</sub>M'<sub>(2-b)</sub>M"<sub>b</sub>P<sub>3</sub>O<sub>12-c)</sub>Z<sub>c</sub>, 0 ≤ b ≤ 2, 0 < c < 12, a is greater than zero and selected to represent the number of Li atoms to balance said formula; where M' and M" are each elements selected from the group consisting of metal and metalloid elements, and said M' and M" are the same or different from one another; and where Z is a halogen.

- 18. The electrode of claim 17 wherein at least one of M' and M" is selected from the group of transition metals, and Z is F (fluorine).
- 19. The electrode of claim 17 wherein M' and M" are each independently selected from the group consisting of transition metals, and Z is F (fluorine).
- 20. An electrode which comprises an active material, represented by the nominal general formula  $\text{Li}_{*}\text{M}'_{(2-b)}\text{M}"_{b}\text{Si}_{y}\text{P}_{3-y}\text{O}_{12-c}\text{Z}_{c}, \text{O} \leq b \leq 2, \text{O} < c < 12, \\ \text{O} \leq y < 3, \text{a is greater than zero and selected to represent the number of Li atoms to balance said formula; where M' and M" are each elements selected from the group consisting of metal and metalloid elements, and said M' and M" are the same or different from one another; and where Z is a halogen.$ 
  - 21. The electrode of claim 20 wherein at least one of M' and M'' is selected from the group of transition metals, and Z is F (fluorine).
    - 22. The electrode of claim 20 where a is 3.